Electron-hole pairs multiquantum generation mechanizm in the process of excitation of $ZnSCdS − Cu$ by an atomic hydrogen

Yu.A.Sivov, Yu.I.Tyurin, V.D.Choruzhii

Tomsk Polytechnical University, Rossia

Abstract

The luminecsence of $ZnSCdS − Cu$ phosphors of various CdS consentration $(0 − 40\%)$ is under investigation. The luminescence was exited by hydrogen atoms during adsorbtion of thermal energy during adsorbtion and impact recombination-heterogeneous chemiluminenscence(HCL) are discussed. The monotone lowering of the conductivity zone bottom level with respect to the valence zone ceiling (from $3,7eV$ to $3,2eV$) with increasing CdS concentration (from $0 − 40\%$). HCL intensity with respect to CdS (from 3,7 eV to 3,2 eV)- concentration (E_g)grows rapidly. The dependence of HCL intensity on the forbidden zone width can be explained by the action of electron - hole pairs multiquontum generation mechanism.

n1. The termal energy atoms and molecules trapped on surface are capable to perform high-frecuency intermolecular and adsorbtional oscillations. The adsorbtion potential depth of chemical active particles on the uviol surfaces variates from $q = 1eV$ up to $10eV$ (the frecuencies correspondingly - from $\omega_0 = 10^{14}s^{-1}$ up to $10^{15}s^{-1}$. One-three photon energy scattering into a crystal is a very effective process near the border of continious energy spectrum. The relaxation rate $\Gamma_{vph} = 10^8 − 10^{11}s^{-1}$ [1, 2]. Having released the energy $\hbar\omega_0 >> kT$ during the time-period $(2 \div 5)\Gamma_{vph}^{-1}$, a particle is caught by the surface, but at the same time it has a large energy exess in its adsorbtion binding $(q − \hbar\omega_0 \geq \hbar\omega_0)$. The following energy release into the crystalline lattice is inhibited by the multiquantum processes $((E_V − E_{vi})/(\hbar\omega_{ph}) \geq 3 \div 5; \Gamma_{vph} = 10^2 \div 10^7 s^{-1}; \hbar\omega_{ph}$-phonon energy). In this case, the nonphonon relaxation processes of energy release into an adsorbtion layer, to ionized surface states, or to the electrons of impurity, Bloch and Tamm states are effective [3, 4].
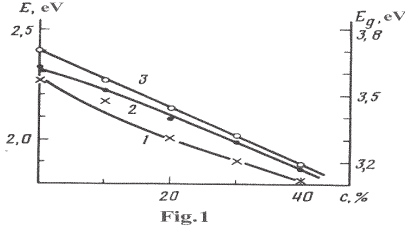
Figure 1: Dependence of the pozition of luminiscence spectrum maxima (1,2) and forbidden zone width (3) of $ZnSCdS - Cu$ phosphor on the CdS concentration; 1- photoluminicence, 2-heterogeneous chemiluminescence in the atomic hydrodgen.
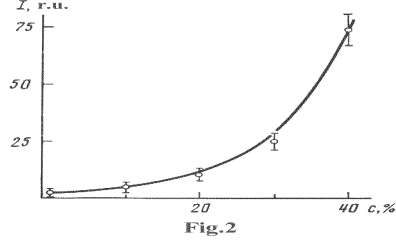

Figure 2: Dependence of the HCL intensits of the $ZnSCdS - Cu$ phosphor on the CdS concentration. Points - are the experimental results, the line represents the theoretical colculations.

The role of the crystal electron states in the energy accomodation process taking place in the gas-surface interaction is widely observed during luminescence of solids located into the active gas medium (free atoms, radicals).This kind of nonequilibrium luminescence is known to be called heterogeneous chemiluminescence HCl [5]. Two modifications of HCL are known: radicalo-recombination and adsorbtion luminescence (RRL and AL) [5] − [7]. RRL is observed in the free atoms recombination process, AL - in the process of adsorption.

n2. This paper presents the experimental results of RRL of $ZnSCdS-Cu$ with the various cosentrations of $CdS(0 - 40\%)$, in the atomic hydrodgen medium. The atomic hydrodgen is produced by dissociation of the molecular hydrodgen during high-frecuency nonelectrode electric charge. In its turn, the molecular hydrodgen is produced by diffusion through a heated palladium.

Kinetic, temperature and spectral characteristic of luminencence are studied with the help of photoelectric amplifier ($PEA - 84$) attached to the output of a high-aperture monochromator, sometimes the interference filters are used.

In Fig.1, position of spectrum maxima of photo and heterogenerous chemiluminescence and the widths of forbidden zone $E_g = E_g(ZnS)[1-C(CdS)]+ E_g(CdS)C(CdS)$ of phosphor $ZnSCdS - Cu$ are given as functions of concentration of $CdS(C(CdS) = 0 - 40\%)$. If can be noted that the rate of spectrum maxima and $E_g(C)$ displayments are practically thesame. HCL

2

intensity with respect to CdS - consentration(E_g decreases) grows rapidly (Fig.2).

For the $ZnSCdS - Cu$ phosphor containing the variable quantities of $CdS(0 - 40\%)$ it is established the Cu^{2+}-centre radiation spectrum is displaced to long wavelength (from $2,4eV$ to $1,9eV$). It is caused by monotone lowering of the conductity zone bottom level with respect to the valence zone ceiling (from $3,7eV$ to $3,2eV$), pozition of the Cu^{2+} - centre with respect to the valence zone ceiling being the same (theory of indirect activation [5]).

The dependence of the RRL intensity of the $ZnSCdS - Cu$ phospor on the CdS concentration can be explained by the action of electron-hole pairs multiquontum generation mechanism.

n3. Because of the oscillation unharmonism and dependence of the dipole (quadrupole) momentum from binding on the internuclear coordinates, the interaction between the oscillotory excited dipole and the crystall elerctron states leads to transmiision of several oscillatory quanta to electrons states at the same time.

If the Morze potential is chosen to describe the unharmonic oscillator, then the rate of the multiquantum oscillatory electron transitions by the zone-zone excitations can be expressed [4] as follows

$$\Gamma_{ev} = \frac{4m_2\theta^2 f(m_r\hbar\omega_0)^{1/2}}{\hbar\omega_0 M m_e E_g}[\frac{\mu(r_0)e(\varepsilon + 2)}{3a^{3/2}\varepsilon}]^2\psi(q/E_g)exp(-\frac{E_g}{\hbar\omega_0}P). \quad (1)$$

Here: m_e - mass of electron, e - elementary electrical charge, $\omega_0 = \alpha(2q/m)^{1/2}$ - oscillator's cyclic frequency, μ - dipole moment of binding, f - oscillatory force, ϵ - permittivity, corresponding to the transmission frequency, q - adsorbtion potential depth, E_g - width of forbidden zone, m_r - equivalent effective mass of an electron - hole pair, a -minimal distance of the energy transportation.

$$\psi(x) = x^2(1 - x^{-1/2})(1 + (2x)^{-1/2}) \quad (2)$$

$$p = z \ln z/(z - 1), z = (4q + \hbar\omega_0)/(E_g + \hbar\omega_0). \quad (3)$$

(1) describes the oscillatory electron transition (inside the static region of a dipole) produced by the dipole interaction of a valence zone electron with the electromagnetic field of an unharmonic oscillator. To describe the dipole - quadrupole interaction, it is necessary to change the expression inside the rectangle parenthesises by $[eD(r_0)/5a^{5/2}]^2$.

The (1) and (3) describing the exitation rate can be used to evaluate the dependence of the phosphor $ZnSCdS-Cu$ luminiscence intensity on the CdS concentration (the width of the phosphor's forbidden zone), (Fig.2). Intensity

of RRL_H depends on the exitation cross - section [9] and is proportional to the rate of the nonequilibrium electron state generation:

$$I \sim \frac{\Gamma_{ev}}{(\Gamma_{ev} + \Gamma_v)(1 + \tau\omega)}(\jmath\sigma_2 N_1 B_{RRL} + \jmath\sigma_1 N B_{Al}. \tag{4}$$

Here: σ_1-adsorbtion cross-section, σ_2 - recombination cross - section, N, N_1 - correspondingly concentration of AL and RPL exitation centres, B_{AL}, B_{RRL} - quantum yield of luminescence outputs of AL and RRL exitation centres, $(1+\tau\omega)^{-1}$ - concentration extinguish factor, $\Gamma_v + \Gamma_{ev}$ - total relaxation rate, $\jmath$ - atom flux density.

These quantities does not (or in a rather small degree) depend on the energy width E_g.

For this situations according $(1-4)$ we get:

$$I_c = a/E_g \Psi(q/E_g)exp(\frac{-E_g}{\hbar\omega_0}P) \tag{5}$$

$$E_g = [3,6 - 1,1C(CdS)]eV \tag{6}$$

where $C(CdS)$ concentration CdS inside the $ZnSCdS - Cu$ phosphor.

The theoretical curve $I(C)$ coincides (in the limits of experimental errors) with the experimental results (see $Fig.2$).($\hbar\omega_0 = 0,32eV, q = 4eV$). The increment of $I(C)$ is not exponential and depends strongly on the factor $(1/E_g)\Psi(q/E_g)$.

When the CdS concentration is great ($C > 60\%$), the HCL output and intensity tend to be lower. It is caused by increasing of the consentration extinguish (factor $(1 + \tau\omega)^{-1}$) and rate of the low - energy relaxation Γ_v of the oscillatory exitation binding $(H - Me^{2+})^v - SU, (H - H)^v - SU$.

References

[1] M.A.Koshushner. //Theoretical problems of chemical physic. M.:"Science", 1982. P.283.

[2] V.P.Zhdanov V.P.,Zamaraev K.I. //Catal.Sci.Eng., 1982. V.24. N3. P.273.

[3] B.R.Shub. Heterogeneous relaxation of reactions chemical internal energy molecules and heterogeneous processes at the solid state surface. Doct. diss. chem. science. M. :Inst.of chem.phys., 1983.

[4] Tyurin Yu.I. //Surface, 1986. N9. P.115.

[5] V.V.Styrov. Energy reactions heterogeneous chemical relaxation with participation of crystall system electrons. Preprint 19-78. Novosibirsk. Inst.of semiconductor physics SO AN SSSR, 1978.

[6] V.A.Sokolov, A.N.Gorban. //Luminescence and adsorbtion. M. :"Science", 1969. P.188.

[7] Yu.N.Ruphov. //Problems of kinetic and catalisys. M.:"Science", 1978. V.17. P.63.

[8] A.M.Gurvisch. Introduction at chemistry physic of crystallophophors. M.:"High.sch.", 1982. P.376.

[9] Yu.I.Tyurin Yu.A., V.V.Styrov V.V. //Chem.phys. 1984. V.3. V.1. P.85.